Design and characterization of late-mixing flash pyrolytic reactor molecular-beam source

Hahkjoon Kim, Kristin S. Dooley, Elizabeth R. Johnson, and Simon W. North*a)

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842

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We report on the design and characterization of an intense pulsed beam source for the generation of expansion-cooled radical species. The source combines both dual pulsed valve late mixing for coexpansion of reactive gases with a pyrolytic end nozzle as a flash kinetic reactor. As a demonstration of the source we present evidence of BrO and ClO radical production and subsequent photodissociation studies of these species using velocity map ion imaging. The radicals are characterized by a rotational temperature of 150±40 K although substantially lower temperatures should be possible. © 2005 American Institute of Physics. [DOI: 10.1063/1.2148991]

Open-shell species play a critical role in chemistry as important intermediates and chain carriers in reacting systems. As a consequence the spectroscopy, thermodynamic properties, and reactivity of radicals have been the subject of numerous experimental and theoretical investigations. Supersonic molecular beams can provide well-collimated, intense sources of expansion-cooled radicals with narrow speed distributions for subsequent study. The design of radical beam sources involves the competition between the requirement for high number density in the interaction region of the vacuum chamber and the desire for minimal interference from unwanted by-products. Since radicals by their nature are highly reactive, the conventional approach has been to produce the radicals rapidly and then limit their residence time within the source in order to minimize recombination and reactive loss prior to expansion.

There have been many studies utilizing flash pyrolytic molecular-beam sources.1 Flash pyrolytic sources rely on the thermal decomposition of a precursor resulting in the desired radical and, if possible, a nonreactive coproduct. The pyrolysis of azomethane (CH₃N₂CH₃) as a source of methyl radicals is a prime example.2–4 The pulsed flash pyrolytic source developed by Zhang et al.,3 Chen and co-workers,5–7 Lee and co-workers,8,9 and Fischer10 has found widespread use in the generation of expansion-cooled radicals. An alternative to the pyrolysis of a single precursor is a high-temperature reaction system capable of producing the radical of interest rapidly and in high yield. Since production of the radicals in this case results from bimolecular reactions rather than from unimolecular decomposition, high partial pressures of the reactants must be employed to ensure rapid conversion to products during the transit time through the nozzle which is typically tens of microseconds.11 Often, mixtures of the reactants at the required partial pressures cannot be prepared or stored. Recently, Camden et al. reported on a late-mixing pulsed nozzle for the coexpansion of reactive gases to circumvent this limitation.12 The source utilized two commercial solenoid valves connected by a 1/16 in. outer diameter (OD) capillary tube to mix the gases during the expansion and the authors demonstrated the utility of the source to the study of photoinitiated reactions, specifically the Cl +CH₃OH reaction. The source described in the present article combines both dual valve late mixing for coexpansion and a pyrolytic nozzle as a flash kinetic reactor. A similar approach has been utilized by Feng et al., employing the photolysis of Cl₂ (rather than pyrolysis) in the presence of methanol to produce CH₂OH radicals.13 The source described in this article is inexpensive, employing commercial pulsed valves and primarily low-cost stock parts for the pyrolytic nozzle, and is sufficiently flexible to generate intense molecular beams of a wide range of chemically interesting radicals.

The pulsed radical beam source assembly shown in Fig. 1 uses two commercial pulsed solenoid valves (Series 9, Parker Hannifin Corporation, General Valve Division) with Teflon poppets. The pulsed valves are seated into custom-machined copper end caps and secured by set screws. A 1.0 mm diameter coaxial channel in both copper end caps serves to connect the pulsed valve orifices through to the outside of the end caps. An additional 1.0 mm diameter channel intersects the first coaxial channel at right angles in the second end cap. A stainless-steel tube approximately 5 cm long [1.0 mm inner diameter (ID) and 1.9 mm OD] connects the front channel of the upper pulsed valve end cap to the top channel of the second pulsed valve end cap (Fig. 1). The lower copper end cap, which serves as a mixing region for the gases, is water cooled to protect the lower pulsed valve from the heated nozzle. The heated nozzle is constructed using a piece of alumina tubing 3.2 cm long with 1.0 mm ID and 2.4 mm OD (Scientific Instrument Services, Inc.). Nickel chromium wire (26 AWG) was tightly wound around the tubing and then sealed with a thin layer of high-temperature ceramic adhesive to achieve uniform heating. The nickel chromium wire was heated using a current-regulated power supply, and nozzle temperatures as a function of power were determined by optical pyrometry.14 The alumina nozzle was then seated into the front of the second pulsed valve at one end and into
a water-cooled copper front plate on the other. The nozzle and front plate are held in place by two threaded rods. The front plate has a 1.0 mm center bore and provides a means of precooling the gas prior to expansion.

As a demonstration of the source we present initial results on the production of BrO radicals. We have previously reported BrO in a molecular beam using a pulsed discharge nozzle\textsuperscript{15} based on a previous design with slight modification\textsuperscript{16–18} although the stability of this source was not amenable to extended signal averaging. The generation of an intense beam of BrO radicals using the current source requires high partial pressure of both reactants. Approximately 30 Torr of O\textsubscript{3} in 760 Torr of He was mixed with 30 Torr of Br\textsubscript{2} in 760 Torr of He prior to expansion through the heated nozzle. The O\textsubscript{3} was trapped over silica gel (3–6 mm, Fluka) at −78 °C and was warmed to −35 °C to achieve the desired vapor pressure. The reaction system includes the following reactions involved in the production of BrO radicals:

\begin{equation}
O_3 + M \rightarrow O_2 + O + M,
\end{equation}

\begin{equation}
Br_2 + M \rightarrow Br + Br + M,
\end{equation}

\begin{equation}
Br_2 + O \rightarrow BrO + Br,
\end{equation}

\begin{equation}
Br + O_3 \rightarrow BrO + O_2.
\end{equation}

Kinetics modeling of the reaction system using a 12-step mechanism suggests efficient conversion of the reactants to BrO during the transit time through the heated nozzle at 600 K.\textsuperscript{19}

Experimental confirmation of BrO radical production was obtained using a molecular-beam velocity map ion imaging apparatus that has been described in detail elsewhere.\textsuperscript{20,21} Briefly, the collimated molecular beam was intersected at 90° by two copropagating linearly polarized laser beams. The dissociation beam was generated using the third harmonic of a Nd:YAG (yttrium aluminum garnet) laser while the probe beam was generated by using the same 355 nm output of the Nd:YAG laser to pump a dye laser operating on the dye Coumarin 500 followed by frequency doubling. Typical dissociation and probe pulse energies were 1 mJ and 50 μJ, respectively. The bromine atoms Br\textsuperscript{2P\textsubscript{3/2}} were probed using 2+1 resonantly enhanced multiphoton ionization (REMPI) transitions at 266.60 nm (3P\textsuperscript{3/2} \rightarrow 4P\textsuperscript{1/2}).\textsuperscript{22} The Br\textsuperscript{+} ions were accelerated by velocity mapping ion optics before entering the 50-cm-long field-free flight tube coaxial with the molecular beam. The ions were projected on a position-sensitive microchannel-plate phosphor assembly gated to detect the mass of interest and a charge-coupled device (CCD) camera acquired images of the phosphor screen which were sent to a computer for analysis. The basis-set expansion (BASEX) method developed by Drinbinski \textit{et al.}\textsuperscript{23} was used in the reconstruction of the three-dimensional (3D) velocity distribution from the ion images.

Figure 2 clearly demonstrates the production of BrO radical using the late-mixing flash pyrolytic reactor. Since the Br\textsubscript{2} + O\textsubscript{3} reaction is very slow at room temperature, a single ring with a radius and anisotropy consistent with the Br\textsuperscript{2} photodissociation at 355 nm is observed with the unheated nozzle.\textsuperscript{24} As the nozzle is heated, an additional ring corresponding to the Br\textsuperscript{2} + O\textsubscript{3} reaction and thermal decomposition of Br\textsubscript{2}. At 600 K the ring due to Br\textsuperscript{2} photodissociation is greatly diminished and the feature associated with Br\textsuperscript{2} photodissociation at 355 nm is evident. The center spot is due to entrained Br\textsuperscript{2P\textsubscript{3/2}} atoms from both the Br\textsuperscript{2} + O\textsubscript{3} reaction and thermal decomposition of Br\textsubscript{2}. At 600 K the ring due to Br\textsuperscript{2} photodissociation is greatly diminished and the feature associated with Br\textsuperscript{2} photodissociation is dominant. Figure 3 shows the speed distributions derived from the images in Fig. 2 as the nozzle is heated. The speed distributions and angular distributions of Br\textsuperscript{2P\textsubscript{3/2}} arising from BrO are consistent with previous reports.\textsuperscript{13} The BrO signal is not observed with either laser beam blocked, either pulsed valve closed, or the probe laser moved off resonance. Based on our kinetics modeling and the relative signal associated with Br\textsubscript{2}
and BrO photolysis we estimate BrO number densities on the order of $1 \times 10^{16}$ cm$^{-3}$ at the source exit can be achieved. A detailed description of the wavelength-dependent photodissociation dynamics of BrO will be the subject of a future publication.25

We have recently reported on the wavelength-dependent photodissociation of ClO using a single pulsed valve flash pyrolytic source to decompose Cl$_2$O. As a further demonstration of the source assembly described in this article, we were able to produce an intense ClO radical beam by mixing Cl$_2$ and O$_3$ in He in a manner analogous to BrO generation. The observed signal intensity using the current source is comparable, perhaps superior, to the signal reported previously and does not require the synthesis and purification of Cl$_2$O.

The rotational temperatures of the radicals using the source was characterized under conditions employed in the BrO and ClO experiments by measuring 1+1 REMPI spectra of NO near 226 nm. A mixture of 5% of NO in 760 Torr of He was passed through both pulsed valves, and the valve opening times and laser delay were identical to the BrO experiments which were optimized for signal-to-noise ratio. Comparison of the NO REMPI spectra with spectral simulations using LIFBASE demonstrated rotational temperatures of 150±40 K. We have typically performed our experiments using the early underexpanded, and hence “warmer,” part of the molecular-beam pulse and also not optimized the source to ensure secondary expansion. We note that significantly colder radical beams can be generated using modified conditions, including higher stagnation pressures (>1 atm) and greater cooling of the front plate.

We anticipate that this inexpensive source is a valuable tool in the production of a variety of expansion-cooled radicals for spectroscopic and chemical dynamics studies.

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14 Nozzle temperatures are limited by the nickel chromium wire although the use of resistively heated silicon carbide tubes as in Ref. 5 could provide significantly higher temperatures if required.
19 We note that quantitative kinetics modeling of the reaction system is non-trivial given both the temperature and pressure gradients within the heated nozzle and the role of wall reactions which are not easily characterized.